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THIRD SERIES—VOLUME LIV—SECTION III
JUNE, 1960

OTTAWA
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PRESIDENTIAL ADDRESS

Group Representations

G. DE B. ROBINSON, F.R.S.C.

> Les mathematiciens n'étudent pas des objets, mais des relations entre les objets; il leur est donc indifférent de remplacer ces objets par d'autres, pourvu que les relations ne changent pas. La matière ne leur importe pas, la forme seule les intéresse.
>
> HENRI POINCARÉ

> The mode of interlocking operations, not their nature, is responsible for those manifestations of the external universe which ultimately reach our senses. According to our present outlook this is the basal principle in the philosophy of science.
>
> SIR ARTHUR EDDINGTON

The theory of groups has become so important a part of physics and chemistry that it seemed a worthwhile topic for our symposium. I thought it desirable, therefore, to present some familiar ideas, but from a slightly different point of view. Representation theory is a tool for the spectroscopist but it is still a fruitful field for mathematical research.

The notion of a group of *permutations* was first introduced by Abel and Galois early in the nineteenth century to provide a criterion for the solvability of algebraic equations by radicals. Not till 1854, however, was the definition of an *abstract* group given by Cayley. We begin by determining all *permutation representations* of a finite group $\mathfrak{G}$. The construction depends on collecting the elements of $\mathfrak{G}$ into *cosets* relative to a subgroup $\mathfrak{H}$:

$$\mathfrak{G} = \mathfrak{H} + \mathfrak{H}A_2 + \ldots + \mathfrak{H}A_n;$$

we assume $\mathfrak{G}$ to be of order g and $\mathfrak{H}$ of order $h < g$. If A_i *is chosen not to lie in any* $\mathfrak{H}A_j$ $(j < i)$, then the assumption that $H_1A_i = H_2A_j$ implies that $A_i = H_1^{-1}H_2A_j$ contrary to supposition, so that $\mathfrak{H}A_i$ *has no element in common with* $\mathfrak{H}A_j$ $(j < i)$. It follows that all the $\mathfrak{H}A_i$ are distinct and $n = g/h$.

Now let us multiply each coset $\mathfrak{H}A_i$ on the right by $G \in \mathfrak{G}$ to obtain some other coset $\mathfrak{H}A_j$. In this way we obtain a *permutation* of the n cosets

$$G \to \begin{pmatrix} \mathfrak{H}A_i \\ \mathfrak{H}A_iG \end{pmatrix}, \quad \text{where} \begin{pmatrix} \mathfrak{H}A_i \\ \mathfrak{H}A_iG \end{pmatrix} \begin{pmatrix} \mathfrak{H}A_iG \\ \mathfrak{H}A_iGG' \end{pmatrix} = \begin{pmatrix} \mathfrak{H}A_i \\ \mathfrak{H}A_iGG' \end{pmatrix},$$

so that these permutations form a *permutation representation* of $\mathfrak{G}$. Since each permutation may be written as a permutation ***matrix***, we have introduced the idea of a ***linear representation*** of $\mathfrak{G}$ in a natural way.

TABLE I

$\mathfrak{H}$	Subgroup	h
$\mathfrak{H}_1$	1	1
$\mathfrak{H}_2$	1, (12)	2
$\mathfrak{H}_3$	1, (12)(34)	2
$\mathfrak{H}_4$	1, (123), (132)	3
$\mathfrak{H}_5$	1, (1324), (12)(34), (1423)	4
$\mathfrak{H}_6$	1, (12)(34), (14)(23), (13)(24)	4
$\mathfrak{H}_7$	1, (12), (34), (12)(34)	4
$\mathfrak{H}_8$	1, (12), (13), (23), (123), (132)	6
$\mathfrak{H}_9$	1, (12), (34), (12)(34), (14)(23), (13)(24), (1324), (1423)	8
$\mathfrak{H}_{10}$	$\mathfrak{A}_4$	12
$\mathfrak{H}_{11}$	$\mathfrak{S}_4$	24

Example. In Table I are listed all subgroups of the symmetric group $\mathfrak{S}_4$. In particular taking $\mathfrak{H} = \mathfrak{H}_8 = \mathfrak{S}_3$ we have (multiplying permutations from right to left):

$$\begin{array}{rccccccc}
 & E_4 & & E_3 & & E_2 & & E_1 \\
\mathfrak{S}_4 = & \mathfrak{S}_3 & + & \mathfrak{S}_3(34) & + & \mathfrak{S}_3(24) & + & \mathfrak{S}_3(14) \\
 & 1 & & (34) & & (24) & & (14) \\
 & (12) & & (12)(34) & & (124) & & (142) \\
 & (13) & & (134) & & (13)(24) & & (143) \\
 & (23) & & (234) & & (243) & & (14)(23) \\
 & (123) & & (1234) & & (1243) & & (1423) \\
 & (132) & & (1342) & & (1324) & & (1432)
\end{array}$$

and

$$(12):\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix},\qquad (23):\begin{pmatrix}1&0&0&0\\0&0&1&0\\0&1&0&0\\0&0&0&1\end{pmatrix},\qquad (34):\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\ldots$$

$$\ldots(12)(34)\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}\ldots(123):\begin{pmatrix}1&0&0&0\\0&0&1&0\\0&0&0&1\\0&1&0&0\end{pmatrix}\ldots(1234)\begin{pmatrix}0&1&0&0\\0&0&1&0\\0&0&0&1\\1&0&0&0\end{pmatrix}\ldots$$

If we denote any one of these permutation matrices by A then the linear transformation $Y = AX$ permutes the basis vectors

$$E_4 = (1,0,0,0),\ E_3 = (0,1,0,0),\ E_2 = (0,0,1,0),\ E_1 = (0,0,0,1)$$

in the same manner as the corresponding permutation of $\mathfrak{S}_4$ permutes their suffixes.

Each subgroup of $\mathfrak{G}$ gives rise to a transitive permutation representation and, conversely, it is easy to prove that every such transitive representation must arise in this way. Finally, every permutation representation arises by combining transitive representations on different sets of symbols.

Since distinct subgroups may have the same order, the *degree* of the representation is not enough to distinguish it. The sum of the diagonal or trace elements is the *character* of the representation and it can be shown that (i) characters of conjugate elements are equal, (ii) characters uniquely determine a representation up to equivalence. Table II gives the characters $\chi_i^{\mathfrak{H}}$ of the different classes in each permutation representation of $\mathfrak{S}_4$, calculated from the formula

$$\chi_i^{\mathfrak{H}} = gg_i^{\mathfrak{H}}/hg_i,$$

where g_i is the number of elements in the ith class and $g_i^{\mathfrak{H}}$ is the number of these which lie in $\mathfrak{H}$.

TABLE II

$\chi_i^{\mathfrak{H}}$

Class	(1^4)	$(2, 1^2)$	(2^2)	$(3, 1)$	(4)
g_i	1	6	3	8	6
$\mathcal{G}_1$	24	.	.	.	.
$\mathcal{G}_2$	12	2	.	.	.
$\mathcal{G}_3$	12	.	4	.	.
$\mathcal{G}_4$	8	.	.	2	.
$\mathcal{G}_5$	6	.	2	.	2
$\mathcal{G}_6$	6	.	6	.	.
$\mathcal{G}_7$	6	2	2	.	.
$\mathcal{G}_8$	4	2	.	1	.
$\mathcal{G}_9$	3	1	3	.	1
$\mathcal{G}_{10}$	2	.	2	2	.
$\mathcal{G}_{11}$	1	1	1	1	1

From the geometrical point of view we might imagine that a change of basis could reveal the existence of an invariant subspace. For example,

$$P(12)P^{-1} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ \hline 0 & 0 & 0 & 1 \end{array}\right), \qquad P(23)P^{-1} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{3}{4} & 0 \\ 0 & 1 & \frac{1}{2} & 0 \\ \hline 0 & 0 & 0 & 1 \end{array}\right),$$

$$P(34)P^{-1} = \left(\begin{array}{ccc|c} -\frac{1}{3} & \frac{8}{9} & 0 & 0 \\ 1 & \frac{1}{3} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \hline 0 & 0 & 0 & 1 \end{array}\right),$$

where*

$$P = \begin{pmatrix} 1 & -\frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \\ 0 & 1 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & 1 & -1 \\ 1 & 1 & 1 & 1 \end{pmatrix}, \qquad P^{-1} = \begin{pmatrix} \frac{3}{4} & 0 & 0 & \frac{1}{4} \\ -\frac{1}{4} & \frac{2}{3} & 0 & \frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{3} & \frac{1}{2} & \frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{3} & -\frac{1}{2} & \frac{1}{4} \end{pmatrix},$$

and $PY = PAP^{-1}$. PX permutes the new basis vectors $PE_4 = (1,0,0,1)$, $PE_3 = (-\frac{1}{3},1,0,1)$, $PE_2 = (-\frac{1}{3},-\frac{1}{2},1,1)$, $PE_1 = (-\frac{1}{3},-\frac{1}{2},-1,1)$. Clearly there are *two* invariant subspaces V_3 and V_1 of V_4, and it can be shown that no further transformation by any P can reduce these subspaces further. The representation of $\mathfrak{S}_4$ in each of V_3 and V_1 is *irreducible*. Such irreducible representations of $\mathfrak{S}_n$ can all be constructed explicitly by Young's theorem *without characters*, and the resulting matrices have been used by Jahn and others in energy calculations. The irreducible characters of $\mathfrak{S}_4$ are given in Table III. Using the well known orthogonality relations between characters,

TABLE III

χ_i^{ρ}

Class	(1^4)	$(2, 1^2)$	(2^2)	$(3, 1)$	(4)
g_i	1	6	3	8	6
[4]	1	1	1	1	1
[3, 1]	3	1	−1	0	−1
$[2^2]$	2	0	2	−1	0
$[2, 1^2]$	3	−1	−1	0	1
$[1^4]$	1	−1	1	1	−1

TABLE IV

$m_\rho^{\mathfrak{H}}$

λ	[4]	[3, 1]	$[2^2]$	$[2, 1^2]$	$[1^4]$
$\mathcal{G}_1$	1	3	2	3	1
$\mathcal{G}_2$	1	2	1	1	.
$\mathcal{G}_3$	1	1	2	1	1
$\mathcal{G}_4$	1	1	.	1	1
$\mathcal{G}_5$	1	.	1	1	.
$\mathcal{G}_6$	1	.	2	.	1
$\mathcal{G}_7$	1	1	1	.	.
$\mathcal{G}_8$	1	1	.	.	.
$\mathcal{G}_9$	1	.	1	.	.
$\mathcal{G}_{10}$	1	.	.	.	1
$\mathcal{G}_{11}$	1	.	.	.	.

---

*We could have chosen P to be orthogonal, but this rational form is required in what follows.

we can find the irreducible components of any linear representation of $\mathfrak{G}$; in particular we can reduce the permutation representations of $\mathfrak{S}_4$ as in Table IV. There is a beautifully simple formula for the multiplicities $m_\rho^{\mathfrak{H}}$ where:

$$\chi_1^{\mathfrak{H}} = \sum_\rho m_\rho^{\mathfrak{H}} \chi_1^\rho, \qquad m_\rho^{\mathfrak{H}} = \frac{1}{h} \sum_{G \in \mathfrak{H}} \chi^\rho(G),$$

which can easily be checked, say in the case of $\mathscr{G}_2$ where $\mathfrak{H}_2 = I + (12)$.

My first new interpretation has to do with Table IV; [3,1] is the group of symmetries of the regular tetrahedron in Figure 1 and I ask the question, how is the geometry of Figure 1 determined from column [3,1] of Table IV?

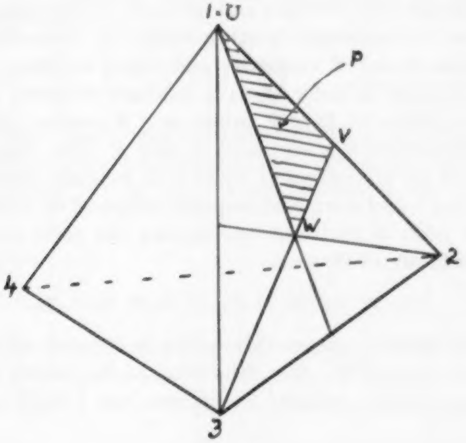

FIGURE 1

Take for example the permutation representation $\mathscr{G}_6$; the four vectors associated with the four cosets form an invariant configuration actually lying in a V_3—namely the space of [3,1]. More generally, the set of 12 vectors on which $\mathscr{G}_2$ is represented is similarly invariant. This set of 12 vectors, or simplex in V_{11}, may be projected down by means of the reduction described above onto each invariant subspace to yield an invariant configuration in that subspace. That [3,1] appears with multiplicity 2 in $\mathscr{G}_2$ means that two independent modes of such projection exist, or, put otherwise, any point in a certain 2-dimensional subspace of [3,1] has a group of stability $\mathfrak{H}_2$. The transformation (12) is a reflection in this subspace which is easily identified as the edge VW of the *fundamental region*. There are 3 such edges in each face of the tetrahedron, making $3 \times 4 = 12 = 24/2$ in all.

If P is internal to the fundamental region, we could apply the transformations of [3,1] to the vector OP and generate a set of 24 vectors permuted according to $\mathfrak{S}_4$. No one of these vectors is left invariant by any transformation but the identity and the number of linearly independent ones is 3 corresponding to the 3 at the head of the column [3,1]. To complete the description of the region we note that $\mathfrak{H}_4 \subset \mathfrak{H}_8$, which yields the vertices U or W of the tetrahedron, while $\mathfrak{H}_3 \subset \mathfrak{H}_7$ yielding the 6 mid-edge points V.

The column headed $[2,1^2]$ yields the geometry of the other 3-dimensional representation of $\mathfrak{S}_4$ corresponding to a subgroup of the group of the octahedron. All the transformations of $[2,1^2]$ are rotations and the fundamental region has its vertices but not its edges completely defined.

The notion of a Kronecker product is of fundamental interest in all applications. This is because in treating symmetry problems one encounters properties which are quite distinct and the order of expressing their respective symmetries is immaterial. In other words, the operations of the corresponding groups $\mathfrak{H}$ and $\mathfrak{K}$ commute and taken together they form the direct product $\mathfrak{H} \times \mathfrak{K}$ of order hk. It is not hard to prove that every irreducible representation of $\mathfrak{H} \times \mathfrak{K}$ arises as a *Kronecker product* $\lambda \times \mu$ of irreducible representation λ and μ of $\mathfrak{H}$ and $\mathfrak{K}$. The character of $\lambda \times \mu$ is the product of the characters of λ and μ. If we insist that $\mathfrak{H}$ and $\mathfrak{K}$ both be $\mathfrak{G}$, that is, that λ and μ are both representations of $\mathfrak{G}$, and limit ourselves to products of pairs of matrices representing the *same* element of $\mathfrak{G}$, we have a representation of $\mathfrak{G}$, since

$$(A_1 \times A_2)(B_1 \times B_2) = A_1B_1 \times A_2B_2.$$

Such Kronecker product representations can be reduced using the character formulae. In the case of $\mathfrak{S}_n$, this reduction can be carried through on the basis of Young's theory without characters, but I shall not pursue this here.

The second new point of view I would like to present to you has to do with the reduction process itself. At the beginning of the paper we showed that for a *proper* choice of P

$$P\,\mathcal{G}_8\,P^{-1} = \left(\begin{array}{c|c} V_3 & 0 \\ \hline 0 & V_1 \end{array}\right).$$

Now it can be proved that such reduction with 0's above *and* below is always possible for finite groups and also for many others, provided the field of coefficients has characteristic zero. $\mathcal{G}_8$ is said to be decomposed into its *indecomposable* components which in this case are also irreducible.

Let us set

$$Q = \begin{pmatrix} 1 & & \\ & 1 & -\tfrac{1}{2} \\ & & 1 \end{pmatrix}, \qquad Q^{-1} = \begin{pmatrix} 1 & & \\ & 1 & \tfrac{1}{2} \\ & & 1 \end{pmatrix}$$

so that, continuing the reduction given above:

$$Q\begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix}\quad Q^{-1}=\begin{pmatrix}1&0&0\\0&1&1\\0&0&-1\end{pmatrix}\equiv\left(\begin{array}{c|cc}1&0&0\\\hline 0&1&1\\0&0&1\end{array}\right),$$

$$Q\begin{pmatrix}1&0&0\\0&-\frac{1}{2}&\frac{3}{4}\\0&1&\frac{1}{2}\end{pmatrix}\quad Q^{-1}=\begin{pmatrix}1&0&0\\0&-1&0\\0&1&1\end{pmatrix}\equiv\left(\begin{array}{c|cc}1&0&0\\\hline 0&1&0\\0&1&1\end{array}\right),$$

$$Q\begin{pmatrix}-\frac{1}{3}&\frac{8}{9}&0\\1&\frac{1}{3}&0\\0&0&1\end{pmatrix}\quad Q^{-1}=\begin{pmatrix}-\frac{1}{3}&\frac{8}{9}&\frac{8}{9}\\1&-\frac{1}{3}&-\frac{1}{3}\\0&0&1\end{pmatrix}\equiv\left(\begin{array}{c|cc}1&0&0\\\hline 1&1&1\\0&0&1\end{array}\right)$$

$$\pmod 2.$$

Here we see the phenomenon which is of such interest to mathematicians. The *modular* representation β:

$$(12):\begin{pmatrix}1&1\\0&1\end{pmatrix}\qquad(23):\begin{pmatrix}1&0\\1&1\end{pmatrix}\qquad(34):\begin{pmatrix}1&1\\0&1\end{pmatrix},$$

which could similarly have been obtained from [2,2], is an irreducible component of the ordinary representation [3,1] (which is thus reducible, though indecomposable (mod 2)). In fact we can construct the "decomposition matrices":

	α	β
[4]	1	
[3,1]	1	1
$[2^2]$	0	1
$[2,1^2]$	1	1
$[1^4]$	1	

$p = 2$

	α	γ	ρ	σ
[4]	1			
$[2^2]$	1	1		
$[1^4]$		1		
[3,1]			1	
$[2,1^2]$				1

$p = 3$

for $p = 2, 3$, in which the modularly irreducible representations are given at the top of each table. In particular for $p = 3$, the representation $[2^2]$ is indecomposable but yet reducible (mod 3) and

$$(12):\begin{pmatrix}1&0\\0&-1\end{pmatrix}\equiv\left(\begin{array}{c|c}1&0\\\hline 0&-1\end{array}\right),\qquad(23):\begin{pmatrix}-\frac{1}{2}&\frac{3}{4}\\1&\frac{1}{2}\end{pmatrix}\equiv\left(\begin{array}{c|c}1&0\\\hline 1&-1\end{array}\right),$$

$$(34):\begin{pmatrix}1&0\\0&-1\end{pmatrix}\equiv\left(\begin{array}{c|c}1&0\\\hline 0&-1\end{array}\right)\qquad\pmod 3$$

splits as indicated in the table; [3,1] and $[2,1^2]$ remain irreducible (mod 3). No such reduction takes place unless p/g so for $\mathfrak{S}_4$, $p = 2, 3$ are the only cases of interest.

The general theory of modular representation was developed in Toronto by Brauer and Nesbitt, 1938–1949. It is difficult to handle in the general case but many of the properties become explicit for $\mathfrak{S}_n$ when Young's theory is modified appropriately. Indeed, the ideas arising in the modular theory have thrown much light on the ordinary theory. An account of these developments is now in the press and should be available next winter.*

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*G. de B. Robinson, *Representation Theory of the Symmetric Group* (to be published).

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Group Representations and Solid State Physics*

W. OPECHOWSKI, F.R.S.C.

Representations of groups play an essential part in physical theories simply because all physical quantities "generate," in a sense to be explained below, some representations of some groups **(1)**. This is true of classical physics as well as of quantum physics, and at any level of sophistication of physical theories. When we say in elementary mechanics that the velocity of a particle is a vector and its kinetic energy a scalar we state in fact which representations of the group of rotations about a point these two physical quantities generate **(2)**. Similarly, the statement that the electric field is a polar vector and the magnetic field an axial vector indicates which representations of the group of inversion these two fields generate.

Although the number of different representations of a group which actually occur in the theories of macroscopic physics is usually small, the situation is quite different in atomic physics. The appropriate language to describe atomic phenomena is quantum mechanics. Here, in general, all irreducible representations of a group are equally important in characterizing the properties of an atomic system. So much so that the mere fact that only one representation of the symmetric group occurs in the quantum mechanical description of a system of identical particles is regarded as a fundamental principle of quantum physics, the so-called Exclusion Principle.

The reason why groups play a *rôle* at all in physical theories is of course the fact that the physical objects, both macroscopic and atomic, manifest certain symmetries.

From the experimental point of view, the essential characteristic of a macroscopic physical object which is "symmetric" with respect to some operation is that there exists no method of ascertaining that the operation has actually been carried out on the object in the past. If you leave a cube on your desk and during your absence somebody turns the cube 90 degrees about an appropriate axis under ideal conditions you will not be able to find out that this happened. This is so because the operation carried out is one of the 23 rotations which together with the identity form a group of operations with respect to which a cube is symmetric.

In the mathematical description of nature as contained in physical theories the fact that certain physical objects are symmetric in the above sense has its counterpart in the fact that certain mathematical expressions are invariant with respect to certain algebraic operations. From the point of view of atomic physics, a physical object is an atomic system which may, of course, be a huge thing like a piece of a solid. In quantum mechanics an atomic system is defined if its Hamiltonian is given. The quantum mechanical Hamiltonian is usually, but not always, obtained by means of certain rules, whose validity is simply postulated, from the Hamiltonian of classical mechanics. Evidently, we cannot carry out symmetry operations on particles constituting an atomic system in the same sense as we can turn a cube lying on a desk; and even in the case of the cube we could not physically carry out any of the reflections with respect to which the cube is, mathematically speaking, symmetric. So that when one speaks loosely, as I did a moment ago, of the symmetry of an atomic system, one really means the invariance of the corresponding Hamiltonian with respect to certain algebraic operations, some of which may not even have a simple geometrical interpretation. However, in so far as a quantum mechanical Hamiltonian can be obtained by a reinterpretation of a classical Hamiltonian these algebraic operations do have a simple geometrical meaning; they are usually rotations, reflections, and translations. It is easy to show that the operations with respect to which a Hamiltonian is invariant always form a group.

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*This paper, along with one by Dr. G. Herzberg on a related topic, constituted with the Presidential Address a Symposium on group theory and its applications.

In many cases the quantum mechanical Hamiltonian is a differential operator operating on complex functions of co-ordinates of the particles which constitute the atomic system, and so giving rise to a partial differential equation, the celebrated Schroedinger equation. Because of the boundary conditions imposed on the solutions, the Schroedinger equation leads to an eigenvalue problem. The eigenvalues are then interpreted in quantum mechanics as the possible values of the energy of the system. Usually there is an infinite number of energy eigenvalues, and to each of them there correspond, in general, several linearly independent eigenfunctions. Now, and this is the crucial point, the linearly independent eigenfunctions belonging to the same eigenvalue "generate" representations of each group with respect to which the Hamiltonian (and hence the Schroedinger equation) is invariant. If one carries out one of the operations of the group on the co-ordinates of the particles which constitute the system —it may be for example a rotation—the Hamiltonian remains unchanged, the eigenvalues also remain the same, but the eigenfunctions after the rotation are different; they are linear combinations of the eigenfunctions obtained before the rotation. Hence, for each energy eigenvalue, a well-defined square matrix of the coefficients in these linear combinations corresponds to the rotation in question. Obviously, we can in this way make a square matrix correspond to each operation of the group, and it is easy to show that the matrices so obtained constitute a representation of the group. The dimension of the representation (that is, the number of rows or columns of any of the matrices of the representation) is equal to the number of linearly independent eigenfunctions belonging to the energy eigenvalue. Energy eigenvalues can thus be characterized by specifying the representations, generated by the corresponding eigenfunctions, of the groups of operations with respect to which the Schroedinger equation is invariant. This fact not only leads very naturally to a fundamental classification of the energy eigenvalues of atomic systems, but also makes it possible to simplify greatly quantum mechanical calculations by invoking various well-known theorems concerning representations of groups. This is also true in those cases in which the basic quantum mechanical equations are more complicated than the Schroedinger equation **(3)**.

Turning now to the *rôle* played by group representations in the quantum theory of solids, I will begin by making a rather trivial remark that, from the atomic point of view, a solid is an extremely complicated thing, and that nobody has yet invented a method of explaining all its properties from a single fundamental point of view. We do have a qualitative, more or less self-consistent atomic description of various kinds of solids and their properties, but when it comes to quantitative explanations we are forced by the complexity of the problem to resort to all kinds of drastic simplifying assumptions which are different for different special problems. Consequently, the group theory aspects of these various problems are not the same either. For example, the usual treatment of the magnetic properties of paramagnetic crystals is based on the assumption that only the symmetry of the immediate environment of paramagnetic ions is of importance, so that no translations appear in the treatment but only rotations and reflections; in other words, from the point of view of group theory, the problem becomes similar to that of a gas of polyatomic molecules. On the other hand, the treatment of the electric and magnetic properties of metals and semi-conductors essentially depends on the symmetry of the solid with respect to translations; in this case, the classical concept of a "perfect crystal" is used with all its implications, and this is why I will mainly be discussing this case.

There are good physical reasons for supposing that to some extent atoms retain their individuality when they form a solid. In particular, it makes good sense to speak of a metal or semi-conductor as consisting of atomic ions and electrons. Atomic ions are several orders of magnitude heavier than electrons. This fact makes it possible to regard the problem as consisting of two somewhat simpler problems which in first approximation can be treated separately. One of them is that of electrons moving in a medium consisting of fixed ions arranged into a three-dimensional geometrical structure symmetric with respect to certain combinations of translations, rotations, and reflections which form one of the so-called "space groups" to be defined in a moment. It is this sort of medium which is a "perfect crystal" of classical atomic physics. The other problem is that of the motion of the ions around the positions which in the first problem were considered to be fixed. In the next approximation one introduces corrections to this somewhat artificial first approximation treatment.

The first problem then is the problem of a huge number of electrons in the presence of forces originating in the fixed ions. This problem is in turn drastically simplified and reduced to the problem of one single electron in the presence of forces originating in the fixed ions and in the remaining electrons. And it is this one-electron problem that I will consider in some detail from the point of view of group theory.

It is necessary first to describe what is meant by a "space group." To this end let us consider the group of all linear transformations of the three Cartesian co-ordinates x_1, x_2, x_3, of a point such that the distance between any two points remains unchanged. Obviously each transformation of the group must be either a rotation about the origin, or a reflection at the origin (an inversion), or a translation of the origin, or finally any combination of these operations. In formulae:

$$x'_1 = R_{11}x_1 + R_{12}x_2 + R_{13}x_3 + t_1,$$

$$x'_2 = R_{21}x_1 + R_{22}x_2 + R_{23}x_3 + t_2,$$

$$x'_3 = R_{31}x_1 + R_{32}x_2 + R_{33}x_3 + t_3,$$

or, using more concise vector notation,

$$\mathbf{r}' = R\mathbf{r} + \mathbf{t},$$

where the absolute value of the determinant of the matrix R is equal to one. In other words, each element of the group is a pair $(R|t)$ of operations of which the first, R, is a rotation or a rotation combined with the inversion, and the second, $\mathbf{t}$, is a translation **(4)**. For brevity I will call the group the "$(R|t)$-group," although it is usually referred to as the "real, inhomogeneous, linear group." The multiplication law of the elements of the $(R|t)$-group is given by the following equation:

$$(R'|t')(R|t) = (R'R|R't + t').$$

The group of "pure translations," $(I|t)$, where I is the unit matrix, constitutes of course a subgroup of the $(R|t)$-group. Consider now a subgroup of this subgroup, consisting of all "primitive translations," $(I|t^{(n)})$, that is of all those translations which are integral linear combinations of three given, linearly independent translations, $\mathbf{t}_1$. $\mathbf{t}_2$, $\mathbf{t}_3$:

$$\mathbf{t}^{(n)} = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3 \qquad (n_1, n_2, n_3 \text{ integers}).$$

For pure translations and, in particular, for primitive translations the group multiplication is simply the vector addition of the elementary vector calculus. The endpoints of the vectors $\mathbf{t}^{(n)}$ form an infinite "lattice."

Now, a "space group" is any subgroup of the $(R|t)$-group such that all its pure translations are primitive, and constitute an invariant subgroup.

It follows almost immediately from this definition that if $(R|t)$ and $(I|t^{(n)})$ belong to a space group then $(I|Rt^{(n)})$ must be one of its primitive translations. This characteristic property of all space groups has an obvious geometrical interpretation (which I will not discuss here), and it implies severe restrictions on the rotations, possibly combined with the inversion, and on the translations which may constitute those pairs $(R|t)$ which form a space group. This is why the number of essentially different space groups is finite. Depending on what is regarded as "essential," there are 219 or 230 of them **(5)**. It should perhaps be stated explicitly that non-primitive translations may very well belong to a space group but only in combination with a rotation about a line or a reflection in a plane; these particular combined operations are called by the crystallographers "screw axes" and "glide planes."

The set of all matrices R, each of which together with a translation constitutes an element of a given space group, form themselves a finite group of rotations (possibly combined with the inversion), which is referred to as the "point group" belonging to the space group. Because of the restrictions imposed on these rotations by the above formulated characteristic property of space groups there are only 32 point groups.

The problem of constructing all the irreducible representations of all space groups has been solved, at least in principle, by Seitz, Wigner, and their collaborators some 20 years ago **(6)**. I say "in principle" because for only a few space groups have the representations been obtained explicitly. The problem is quite involved, and I cannot discuss it here. The only thing I can do is to show how the representations of a space group and especially those of the subgroup of primitive translations, appear in the quantum mechanical treatment of the case of an electron in a perfect crystalline medium.

If we disregard any characteristics of an electron other than its mass and electric charge, the Hamiltonian for this case will be invariant with respect to some space group. The linearly independent solutions of the corresponding Schroedinger equation will then generate a representation of that space group, and hence, of any of its subgroups. In particular, if $\mathbf{r}$ is the position vector of the electron, and $\mathbf{k}$ an arbitrary, fixed real vector, each solution $\psi_k(\mathbf{r})$ of the form

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_k(\mathbf{r})$$

generates a one-dimensional (and, hence, trivially irreducible) representation of the subgroup of primitive translations $\mathbf{t}^{(n)}$, provided $u_k(r)$ is a function invariant under primitive translations:

$$u_k(\mathbf{r} + \mathbf{t}^{(n)}) = u_k(\mathbf{r}).$$

The eigenfunctions $\psi_k(\mathbf{r})$ of this form are called "Bloch functions" **(7)**; they describe modulated plane waves, the vectors $\mathbf{k}$ being "wave vectors." In fact, if we carry out a primitive translation, that is, if we replace $\mathbf{r}$ by

$\mathbf{r} + \mathbf{t}^{(n)}$ in a Bloch function, the function is simply multiplied by $e^{i\mathbf{k}\cdot\mathbf{t}^{(n)}}$. To each primitive translation there corresponds in this way an unambiguously defined complex number, and the set of all these complex numbers (which can be regarded as matrices of one row and one column) constitutes a one-dimensional representation of the group of primitive translations.

To each vector $\mathbf{k}$ there corresponds one such representation, but they are not all different. For

$$e^{i\mathbf{k}\cdot\mathbf{t}^{(n)}} = e^{i\mathbf{k}'\cdot\mathbf{t}^{(n)}}$$

if

$$\mathbf{k}' = \mathbf{k} + 2\pi\mathbf{g},$$

and the vector $\mathbf{g}$ is such that $\mathbf{g}\cdot\mathbf{t}^{(n)}$ is an integer for all $\mathbf{t}^{(n)}$; in other words $\mathbf{k}$ and $\mathbf{k}'$ define the same representation. This mathematical fact has a simple physical interpretation. To see this, we first rewrite the condition for two wave vectors to define the same representation as follows:

$$(\mathbf{k}' - \mathbf{k})\cdot\mathbf{t}_i = 2\pi g_i \qquad (i = 1, 2, 3),$$

where g_1, g_2, g_3 are integers. Next, we specialize this condition by assuming that the magnitudes of the wave vectors $\mathbf{k}$ and $\mathbf{k}'$ are equal; it can then be replaced by the following set of three equations,

$$(\mathbf{s}' - \mathbf{s})\cdot\mathbf{t}_i = \lambda g_i \qquad (i = 1, 2, 3),$$

if use is made of the relation between a wave vector k and the corresponding wave-length λ, namely, $\mathbf{k} = 2\pi\mathbf{s}/\lambda$, where $\mathbf{s}$ is a unit vector. The three equations are nothing but the celebrated conditions of Von Laue for diffraction of waves by a perfect crystal: if $\mathbf{s}$ defines the direction of propagation of an incident wave, $\mathbf{s}'$ the direction of propagation of a wave scattered without change of the wave-length, then the intensity maxima of the diffraction pattern occur along the directions $\mathbf{s}'$ which satisfy the three equations. Von Laue established in 1912 his diffraction conditions for the case of electromagnetic waves (X-rays); we discuss here matter waves (De Broglie waves). The conditions for diffraction maxima are in both cases the same because what really determines their validity is the fact that in both cases the quantities which describe the waves generate the same representations of a group of primitive translations.

One can formulate the diffraction conditions in still another manner. If one understands by the "state" of an electron in a crystalline medium its Bloch function, then the diffraction conditions can be stated simply by saying that the initial and final state of the electron must generate the same representation of the group of primitive translations characterizing the medium. In this form the diffraction conditions become a special case of a rule of a very general validity in quantum mechanics. The rule says that the initial and final state of any physical system must generate the same irreducible representation of the group with respect to which the

Hamiltonian of the system is invariant; of course, the terms "initial state" and "final state" must be appropriately defined. The practical value of this rule in quantum mechanical calculations is great. Its various formulations, adapted to various special cases, are called "selection rules."

The fact that two different wave vectors may define the same representation of the group of primitive translations gives rise to two fundamental concepts of solid state physics: the concept of "reciprocal lattice," and that of "Brillouin zone." It is easy to see that the set of all vectors $\mathfrak{g}$ introduced a moment ago is another group of primitive translations; the corresponding lattice is called "reciprocal lattice" **(8)**. Thus, each ("direct") lattice has its reciprocal lattice. One also introduces the term "reciprocal space" for the continuum of points among which those which are the endpoints of vectors $\mathfrak{g}$ form the reciprocal lattice. Every point of the reciprocal space can be interpreted as the endpoint of a wave vector $\mathbf{k}$, and for this reason the reciprocal space is also called the "k-space." It is possible to define a region in the k-space such that any two points inside this region correspond to two different representations of the group of primitive translations in the direct space, and no point outside the region corresponds to a representation which would not have also a corresponding point inside the region or on its boundary. In other words, no points outside the region give rise to new representations. Moreover, this region can always be chosen such that it has the shape of a polyhedron which has the symmetry of the point group belonging to the space group in question. This symmetric polyhedron in the k-space is called the "Brillouin zone" **(9)**. Evidently, each Bloch function corresponds to some point of the interior or boundary of the Brillouin zone. In fact, one can deduce from the Schroedinger equation that infinitely many Bloch functions correspond to each point of the Brillouin zone; they belong, in general, to different eigenvalues of the energy of the electron, but there exist important exceptions. Several Bloch functions which correspond to different points of the Brillouin zone very often belong to the same energy eigenvalue. They necessarily generate a representation of the whole space group.

A different description of the situation is obtained by introducing the concept of "energy bands" of an electron **(10)**. We have seen that to each point of the Brillouin zone there corresponds an infinity of energy values of the electron. In other words, the energy of the electron is a multivalued function, $E(\mathbf{k})$, of $\mathbf{k}$ defined over the Brillouin zone. A branch of this function is called "energy band." The properties of a metal or a semiconductor are determined, in so far as they depend on its electrons, by these energy bands. The structure of the energy bands, that is, the structure of the hypersurface $E(\mathbf{k})$ with its infinitely many sheets, is obviously closely connected with the properties of those representations of the space group which are generated by the eigenfunctions of the electron, and this is why these representations are of such a great interest to solid state physicists **(11)**.

In the preceding discussion I have entirely disregarded the fact that an electron has not only a mass and a charge, but also an intrinsic angular momentum, the "spin," and a magnetic moment associated with the spin. I have already said before that when one speaks loosely of the symmetry of an atomic system in quantum mechanics one really means the invariance of the corresponding Hamiltonian with respect to a group of algebraic operations which may not have a geometrical interpretation in ordinary three-dimensional space. In particular, such a simple geometrical interpretation is impossible in the case of the quantum mechanical Hamiltonian of any elementary particle with spin. More specifically, for an electron with spin in a perfect crystalline medium, the symmetry of the problem is no longer characterized by a space group, but by a so-called "double space group," and the Hamiltonian is invariant under the operations constituting a double space group rather than a space group. Given a space group, the corresponding double space group is unambiguously determined. Again, only for a few double space groups the irreducible representations have been discussed in some detail **(12)**.

In many solid state phenomena the dynamical *rôle* played by the electron spin is secondary, but the most recent work on the structure of energy bands in metals and semi-conductors does take into account the complications arising from the fact that the true symmetry of the Hamiltonian is characterized by a double space group rather than by the corresponding space group **(13)**.

While the electric and magnetic properties of such solids as metals and semi-conductors are determined mainly by the electronic energy band structure, the thermal properties of all solids depend essentially on the motion of atomic ions. In fact, it is the average energy of the ions which almost completely determines the temperature of a solid.

A basic assumption made concerning the motion of the ions is that they remain in the close vicinity of those points ("equilibrium positions") which I supposed to be fixed in the preceding discussion. More specifically, one assumes, classically speaking, that the ions carry out small oscillations about the equilibrium positions **(14)**. The results of the quantum mechanical treatment of these oscillations are usually expressed in a manner which has its deeper justification again in the group theoretical aspects of the problem.

The Hamiltonian of the system of ions, and hence the Schroedinger equation, is again supposed to be invariant with respect to a space group. As in the case of an electron in a crystalline medium, one introduces quantities which generate one-dimensional representations of the subgroup of primitive translations. In the case of the electrons these quantities were the Bloch functions; here they are essentially the Fourier transforms of the deviations of the ions from their equilibrium positions. As previously, each representation $e^{i\mathbf{q}\cdot\mathbf{t}^{(n)}}$ is characterized by a vector which is here usually denoted by $\mathbf{q}$. And, of course, we can again define a Brillouin zone in the

q-space. In the case of an electron the wave vector **k** specifies not only the direction of propagation of a modulated plane wave, but also—if we use the "particle language" instead of the "wave language"—the direction of motion of the electron. Hence, the group theoretical analogy between the present problem and the problem of an electron in a perfect crystalline medium makes it possible to interpret the vector **q** as specifying the direction of motion of a particle which is called a "phonon" **(15)**. For the most part, I must ignore the fact that a phonon is, apart from the analogy just formulated, quite a different kind of particle from an electron. I can, however, mention two points.

First, although in the case of an electron without spin its possible energy values could be given by introducing one multivalued function, $E(\mathbf{k})$, defined over a Brillouin zone, here it is necessary to introduce several such multivalued functions, $E_s(\mathbf{q})$, where the index s serves simply to label them. For a given phonon, the index s is said to specify its "polarization state."

However, and this is the second point, these functions $E_s(\mathbf{q})$ are trivially multivalued: for any given point of the Brillouin zone, and any one given multivalued function, the consecutive values of the function differ by a constant. For this reason it is possible and customary to assign to a phonon with a given **q** and s an energy equal to this constant. The various eigenstates of the system of ions can then be specified by listing the number of phonons for each pair of the quantities **q** and s. And the temperature of a solid is characterized by the average numbers of phonons with a specified direction of motion, polarization, and energy.

REFERENCES

1. The term "representation" of a group will always mean in this paper a representation by matrices whose elements are complex numbers. The definition of this term and of several other terms used in the theory of groups can be found in G. de B. Robinson's Presidential address in this issue.
2. The term "vector" as used in physics (and, occasionally, in this talk) has also often a different meaning, the meaning it has in the phrase "abstract vector spaces."
3. E. P. Wigner was the first to recognize fully the importance of representations of groups in quantum mechanics. Cf. his two classic papers, Z. Physik, *40* (1927), 883, and *43* (1927), 624.
4. The $(R|t)$ notation, which is commonly used by the physicists, was introduced by F. Seitz, Z. Kristallogr., *91* (1935), 336.
5. The complete enumeration of all space groups is due to the independent work of three men, E. S. Fedorov, A. M. Schoenflies, and W. Barlow, towards the end of the nineteenth century. A brief historical account of the efforts culminating in this work is given, for example, in G. F. Koster's review article "Space Groups and Their Representations," Solid State Physics, *5* (1957), 173.
6. F. Seitz, Ann. Math., *37* (1936), 17; L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, Phys. Rev., *50* (1938), 58; C. Herring, J. Franklin Inst., *233* (1942), 525. Cf. also G. F. Koster, "Space Groups and Their Representations," Solid State Physics, *5* (1957), 173, and chapter VI of J. S. Lomont, *Applications of Finite Groups* (New York and London: Academic Press, 1959).

7. F. Bloch, Z. Physik, *52* (1928), 555; cf. also E. E. Witmer and L. Rosenfeld, Z. Physik, *48* (1928), 530.

8. P. P. Ewald, Ann. Physik, *54* (1917), 519 and 557.

9. Léon Brillouin, *Quantenstatistik* (Berlin: Springer, 1931).

10. F. Bloch, Z. Physik, *52* (1928), 555.

11. Cf., for example, F. Herman's review article "Theoretical Investigation of the Electronic Band Structure in Solids," Revs. Mod. Phys., *30* (1958), 192.

12. The term "double group" was introduced by H. A. Bethe, Ann. Physik, *3* (1929), 133, in connection with point groups; cf. also W. Opechowski, Physica, *7* (1940), 552, and R. J. Elliott, Phys. Rev., *96* (1954), 280.

13. Cf. F. Herman, "Theoretical Investigation of the Electronic Band Structure in Solids," Revs. Mod. Phys., *30* (1958), 192.

14. I think it is right to regard the paper by M. Born and Th. von Karman, Physik. Z., *13* (1912), 297, as the starting point of all modern work on this problem. A review of the present state of the problem in its quantum mechanical form can be found in J. M. Ziman, *Electrons and Phonons* (Oxford: The Clarendon Press, 1960).

15. So far as I know, the term "phonon" was introduced by J. Frenkel some 30 years ago.

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SECTION III

Some Problems in the Kinetics of Electrochemical Reactions

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1. Introduction. A number of problems which are peculiar to the field of electrochemical kinetics are encountered in the study of reactions involving charge transfer between phases differing in electric potential. It is the purpose of this paper to examine first the nature of some of these problems in relation to the kinetics of ordinary heterogeneous processes and then to refer to recent work on certain reactions in order to exemplify the principles and problems involved.

2. Formulation of kinetic equations. The formulation of kinetic equations for electrochemical reactions differs from that for ordinary homogeneous or heterogeneous reactions in the following ways.

(i) Rates can be measured and expressed most conveniently in terms of current i which is directly proportional to the actual reaction velocity v expressed, for example, as moles of product formed per second per square centimetre of electrode surface; thus

$$i = zFv \tag{1}$$

if z Faradays are involved in the production of one mole of product per sec per cm^2 in, for example, the forward direction of the reaction. In relating i to v, current efficiencies must be evaluated unless the reaction product is unambiguous, for example, in the cathodic evolution of hydrogen at metals from acid solutions. In many cases the current efficiency can be less than unity, for instance, in cathodic deposition of metals less noble than hydrogen, in anodic oxygen and halogen evolution where some attack of the metal may be an attendant process, and in the Kolbe reaction **(1; 2)** where not only some dissolution of the metal occurs but the chemical nature of the reaction products varies with current density and temperature **(1)**.

(ii) The rate is not a unique function of concentration of reactants, temperature, surface conditions, etc., but is dependent on the electric potential difference across the interface at which the transfer of charge occurs. Since the reactants are charged and the final products usually uncharged or dipolar, there can be a variation of electrochemical potential (used in the sense of Guggenheim **(3)**) of the initial state of the reaction (ions in solution at the interface, electrons in the metal) with the absolute electrical metal-solution p.d. $\Delta\phi$ at the interface and this causes a variation of the standard electrochemical free energy of activation $\Delta\bar{G}^{0\ddagger}$ with $\Delta\phi$ as expressed in equation (2) below.

Generally, for a z-electron charge transfer process,

$$(2)^* \qquad \Delta\bar{G}^{0\ddagger} = \Delta G^{0\ddagger} + z\beta(\Delta\phi - \zeta)F$$

where $\Delta\phi - \zeta$ $(= \Delta V)$ is the potential difference between the metal and the layer of adsorbed ions about to undergo reaction, ζ the potential of this layer with respect to that of the bulk of the solution and β is a factor (usually *ca.* 0.5) determined by the symmetry of the potential energy barrier for the electrochemical charge-transfer reaction and indicates approximately that fraction of ΔV through which the charge must be transferred to reach the transition state from the initial state of the reaction; $\Delta G^{0\ddagger}$ is the value of the free energy of activation when $\Delta V = 0$.

(iii) The activity of reactant ions at the interface must be expressed in terms of the activity in the bulk. This is analogous to the case of heterogeneous reactions where the surface concentrations must be related to those in the bulk through, for example, a Langmuir or Temkin isotherm, the conditions of pressure or concentration then determining in part the kinetic order of the reaction. Usually we can write (cf. **6**) for ions i an electrostatic isotherm of the form

$$(3) \qquad (a_i)_{\text{surface}} = \kappa(a_i)_{\text{bulk}} \exp(-z\zeta F/RT)$$

where $z\zeta F$ is the difference of electrostatic free energy of the ions in the bulk and in the adsorbed layer at the surface and κ is the thickness of the adsorbed layer and normalizes the difference of units used for expressing the surface and the bulk activities. In the case of specifically adsorbed ions, for which $(a_i)_{\text{surface}} \neq (a_i)_{\text{bulk}}$ when $\zeta = 0$, other "chemical" free energy factors enter into the determination of the electrochemical free energy of adsorption but there is no advantage, in principle, in distinguishing between the chemical and electrostatic factors in adsorption of the ions nor is such a distinction possible except at the potential of the electrocapillary maximum of the metal.

(iv) The terms in equations (1), (2), and (3) may now be combined to give the basic kinetic equation for the current i as

$$(4) \quad i = zF\frac{kT}{h}\tau(a_i)_{\text{surface}}(1-\theta)\exp\left\{-[\Delta G^{0\ddagger} + z\beta(\Delta\phi - \zeta)F]/RT\right\}$$

where θ is the fraction of the metal surface covered with products of the ionic discharge reaction and other terms not previously defined have their usual significance (**4**). It will be observed that i is determined by θ and ΔV in addition to the factors already mentioned. The latter term is not, in principle, determinable (cf. **3**) since it refers to an absolute single p.d.

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*This simplified expression summarizes the main factors determining $\Delta\bar{G}^{0\ddagger}$. More generalized expressions having a similar form have been given in other papers (**4**; **5**).

between two phases; in certain cases θ can be estimated from galvanostatic d.c. charging or discharging curves **(7)**; in limiting cases it may tend to zero or unity.

The problem of the inaccessibility of $\Delta\phi$ is usually avoided by expressing equation (4) in terms of the overpotential η where $\eta = \Delta\phi - \Delta\phi_r$ and $\Delta\phi_r$ is that value of $\Delta\phi$ at the interface when the reaction occurring there is in thermodynamic equilibrium. The rate can then be written as

$$(5)\quad i = \left\{zF\frac{kT}{h}\tau\,.\,\exp - [z\beta F\Delta\phi_r/RT]\,.\,\exp - [\Delta\zeta^{\ddagger}/RT]\right\}(a_i)_{\text{bulk}}(1-\theta)$$

$$\exp - [z\zeta F(1-\beta)/RT]\,\exp - [\beta zF\eta/RT].$$

For a given metal and temperature, the terms inside the curly bracket are a constant K but $\Delta\phi_r$ is strictly still unknown. The current i (or i_0 when $\eta = 0$) can, however, be measured easily and is an exponential function (the "Tafel" equation) of η as indicated by equation (5).

3. Reaction mechanism and slopes of Tafel lines. For a simple ionic neutralization process, $d\eta/d\ln i$ is given directly from equation (5) as $-RT/\beta zF$. However, in many cases, reactions subsequent to the charge transfer step can be rate-determining and lead to values of $d\eta/d\ln i$ which differ from that given above.

In the case of cathodic hydrogen evolution the following pathways have been considered (**4**; **5**; **8**; **9**; **10**; **11**):

Simple Discharge $H_3O^+ + e_M + M \rightarrow MH + H_2O$ I

(or in alkali) $H_2O + e_M + M \rightarrow MH + OH^-$ Ia

followed by *either* of the alternative processes shown below:

Ionic Desorption $H_3O^+ + e_M + MH \rightarrow H_2$ II

(or in alkali) $H_2O + e_M + MH \rightarrow H_2 + OH^-$ IIa

or desorption by

Atomic Recombination $MH + HM \rightarrow H_2.$ III

In the above scheme, I (or Ia) is always a necessary primary step which is followed *either* by II or III. The following reactions involving the hydrogen molecule-ion:

$H_3O^+ + MH \rightarrow M{-}H_2^+$ [Heyrovsky **(9)**] IV

and

$M{-}H_2^+(H_2O) + e_M \rightarrow H_2$ [Horiuti **(11)**] V

have also been considered as possible rate-determining steps but have received either little support **(12)** or their kinetic consequences have not been examined in detail (cf. **4**; **5**).

The kinetic equations for II and III, analogous to that for I, are:

$$i = 2Fk_2(a_i)_{\text{bulk}}k'\theta_H \exp -[\beta F\eta/RT] \tag{6}$$

and

$$i = 2Fk_3(\theta_H)^2 \tag{7}$$

respectively, where k_2 and k_3 are electrochemical rate constants and k' is another term constant at constant electrolyte concentration. Application of the steady state hypothesis with regard to H atom concentration to reaction I followed by rate-determining II, *or* to reaction I followed by rate-determining III enables θ_H to be evaluated as a function of potential. Insertion of θ_H into equations (6) or (7) and taking $\beta \doteqdot 0.5$ then gives (cf. **4**) for II, $d\eta/d\ln i = -2RT/3F$ $(\theta \ll 1)$ or $d\eta/d\ln i = -2RT/F$ $(\theta \rightarrow 1)$, and for III $d\eta/d\ln i = -RT/2F$ $(\theta \ll 1)$ or $d\eta/d\ln i = \infty$ $(\theta \rightarrow 1)$. The limiting values of the slopes $d\eta/d\ln i$ are thus, in some cases, characteristic of reaction mechanism. The value $-RT/2F$ found **(13; 36)**, for example, for cathodic polarization of activated platinum and palladium (at low current density) uniquely indicates III as rate-determining. However, values of $d\eta/d\ln i$ equal to $-2RT/F$ are found at many metals **(4)** and it is therefore impossible, without further evidence, to state the rate-determining mechanism in these cases; further criteria of an indirect nature will therefore be considered in a subsequent section.

The possibility **(9; 11)** that the formation or neutralization of an adsorbed H_2^+ ion may be involved in cathodic hydrogen evolution may be regarded as equivalent to considering the "activated state" of II as a separate entity having appreciable stability and lifetime. The pathway in over-all H_2 production in this case would be

$$H_3O^+ + e_M + M \rightarrow MH \qquad \text{I}$$

$$MH + H_3O^+ \rightarrow MH_2^+(H_2O) \quad \text{[Heyrovsky*]} \qquad \text{IV}$$

$$MH_2^+(H_2O) + e_M \rightarrow H_2 \quad \text{[Horiuti].} \qquad \text{V}$$

Reactions IV and V have been written **(5)**:

$$M + 2H^+ + e_M \rightarrow H_2^+M; \quad H_2^+M + e_M \rightarrow H_2.$$

However, this formulation implies the simultaneous interaction of two protons in the first step so that the reactions probably would really proceed through the initial discharge of one proton followed by a second proton transfer (without neutralization) to give adsorbed H_2^+ as we have shown above; the adsorbed H_2^+ ion is then neutralized by an electron. We cannot assume that the rate of the proton transfer step IV is not dependent upon

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*In 1925 this was formulated by Heyrovsky as $H^+ + H^- \rightarrow H_2$ and the reaction shown above was later proposed by him in 1937 **(9)**. Neither of these steps is strictly the same as the electrochemical desorption or "atom-ion" reaction II which has been referred to as the "Heyrovsky" reaction by some authors **(32)**.

ΔV since (a) it will be an activation controlled step and (b) some transfer of the proton down the potential gradient ΔV must presumably occur.

Following the formation of MH in I, the further proton transfer with eventual neutralization will occur across the potential drop ΔV. If the proton falls through a fraction γ of ΔV in step IV then it will fall through $(1 - \gamma)\Delta V$ in step V. Let β_1, β_4 and β_5 be the symmetry factors corresponding to these steps.

Case (i). *V rate-determining, I and IV in quasi-equilibrium.** The rate v_5 is given by

$$i_5 = zFv_5 = zFk_5a_{\mathrm{MH_2^+}} \exp -[\beta_5(1 - \gamma)\Delta VF]/RT; \tag{8}$$

also

$$a_{\mathrm{MH_2^+}} = K_4a_{\mathrm{MH}}a_{\mathrm{H^+}} \exp(-\gamma\Delta VF/RT) \tag{9}$$

and for step I almost in equilibrium and

$$\theta_{\mathrm{MH}} < \theta_{\mathrm{MH_2^+}} < 1$$

$$a_{\mathrm{MH}} = K_1a_{\mathrm{H^+}} \exp(-\Delta VF/RT) \tag{10}$$

so that

$$a_{\mathrm{MH_2^+}} = K_4K_1(a_{\mathrm{H^+}})^2 \exp[-(1 + \gamma)]\Delta VF/RT \tag{11}$$

where the capital K's are the equilibrium constants for the steps indicated by the subscripts and k_5 is the rate constant for V. Hence

$$i_5 = 2Fk_5K_4K_1(a_{\mathrm{H^+}})^2 \exp -[\beta_5(1 - \gamma) + 1 + \gamma]\Delta VF/RT. \tag{12}$$

With $\beta_5 = 0.5$ and $d\eta/d \ln i = d\Delta V/d \ln i$,

$$d\eta/d \ln i = -2RT/(3 + \gamma)F.$$

At high potentials when $\theta_{\mathrm{H_2^+}} \rightarrow 1$ and is independent of ΔV, $d\eta/d \ln i$ of course becomes $-2RT/(1 - \gamma)F$.

Case (ii): *IV rate-determining, I in quasi-equilibrium.* Here

$$i_4 = Fk_4a_{\mathrm{MH}} \cdot a_{\mathrm{H^+}} \exp -[\beta_4\gamma\Delta VF/RT]. \tag{13}$$

When $\theta_{\mathrm{H}} < 1$ and $f(\Delta V)$, and $\beta_4 = 0.5$

$$d\eta/d \ln i = -2RT/(2 + \gamma)F;$$

when $\theta_{\mathrm{H}} \rightarrow 1$ and is independent of ΔV, $d\eta/d \ln i = -2RT/\gamma F$. The hydrogen molecule ion mechanism can therefore give a variety of slopes depending upon the extent of transfer of the proton across the double-layer in step IV. Rate-determining IV gives $d\eta/d\ln i = -RT/F$ when $\gamma = 0$, or $-2RT/3F$ when $\gamma = 1$ (the process then becomes virtually identical with rate-determining II); similarly for rate-determining V, $d\eta/d\ln i = -2RT/3F$ for $\gamma = 0$ and $-RT/2F$ for $\gamma = 1$ when $\theta_{H_2^+} \ll 1$. The condition $\gamma = 0$ could only correspond to "sideways" transfer of a proton to MH in the double-layer and correspondingly a value of γ equal to unity is unlikely since this would correspond to complete proton transfer across ΔV without neutralization by the "excess electron" in the metal.

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*In this treatment we have regarded steps preceding the rate-determining step as almost in equilibrium and obtained the Tafel slopes for limitingly low or high coverages of the surface by one or other of the possible intermediates (cf. **37**). With these assumptions the steady state method can be shown (e.g., see **38**) to lead to the same results as those obtained using the quasi-equilibrium hypothesis.

It is of interest to note that at high potentials where $\theta_{H_2^+} \rightarrow 1$ or $\theta_H \rightarrow 1$ the Tafel slope can become numerically *greater* than $2RT/F$. Thus if γ were 0.5 and under the above conditions of $\theta_{H_2^+}$ or θ_H, IV and V will both give $d\eta/d\ln i = -4RT/F$. Hitherto it has been difficult to explain on any mechanism the high slopes which are often observed in impure solutions, for instance, at Pb where $b = 0.28$ has been recorded **(39)**. Anomalous increases of slope with time to values above $2RT/F$ also occur in impure solutions and upon repetitive polarization.

The existence of H_2^+ as an adsorbed species in the chemisorption of hydrogen at metals has been proposed on the basis of surface potential measurements by Mignolet **(14)** and received some support from the work of Sachtler **(15)** on resistance of surface films of nickel on which hydrogen is chemisorbed. The slow neutralization of adsorbed H_2^+ is, however, unlikely to be rate-determining at Hg (cf. **12**) since chemisorbed species are undetectable **(16)** at this metal. The possibility of reaction V occurring at transition metals under high purity conditions is again unlikely since the slopes observed $(-2RT/F)$ in most cases could only be explained if γ were zero and $\theta_{H_2^+} \rightarrow 1$, that is, if there were no transfer of the proton across the potential gradient in step IV. The slopes derived by Parsons **(5)** for IV and V must be regarded as special cases of the above scheme; thus, in his treatment, the formation of H_2^+ is considered to occur in one step involving the unlikely simultaneous interaction of two hydrated protons; the two-stage *consecutive* pathway considered above would appear to be more likely.

4. Changes of slope of Tafel lines. At some metals sharp changes of slope of the $\eta - \ln i$ lines are observed. In these cases a change of mechanism is indicated **(21)** and from the *direction* of the change of slope, for example from high to low, or from low to high values with increasing current density, the type of sequence of steps in the over-all mechanism can be deduced. Thus, for example, in Figure 1 we may consider consecutive reactions as shown in the upper diagram; at any potential the process passing the smaller current will limit the over-all rate. If two possible steps are involved which are *consecutive* in the over-all reaction and they are associated with different Tafel slopes, then the process with the higher slope $d\eta/d\ln i$ will pass the smaller current at higher potentials and hence be rate-determining and there will be a "concave" inflection in the polariza-

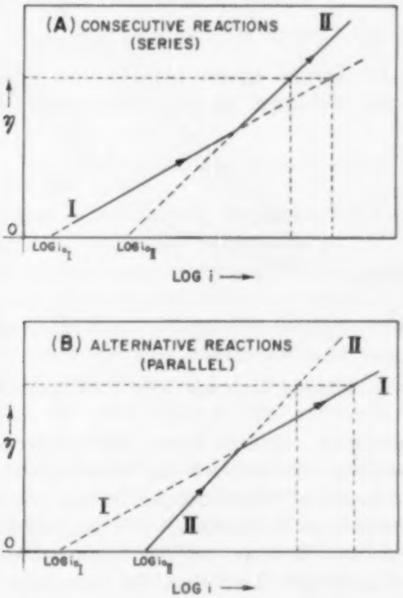

FIGURE 1. Changes of slope and reaction mechanism. *Top*: Process I is slower than II but its rate depends more on potential than does that of II. At high potentials II becomes rate-determining even though $i_{0_{II}} > i_{0_I}$. *Bottom*: At high potentials, if I and II are alternative, I passes more current than II even though $i_{0_I} < i_{0_{II}}$.

tion line. Conversely (see lower diagram of Figure 1), there is a "convex" inflection when in an alternative reaction scheme (e.g., for desorption of adsorbed H atoms) one process can become faster than the other and hence is kinetically predominant with increasing potential. Both types of inflection have been observed in hydrogen **(17; 18)** and oxygen evolution reactions **(19; 20)** and when they occur useful supplementary information on the sequence of reaction mechanisms can be deduced. An example is shown in Figure 2 for the hydrogen and deuterium evolution reactions **(36)** at Pd where the slopes change from $-RT/2F$ (rate-determining III) to $-2RT/F$ as the current density is increased. The change of mechanism must hence be from III to I (or Ia) and not from III to II.

5. Heats of activation and frequency factors. In electrochemical kinetics, evaluation of the apparent heat of activation $\Delta H^{\neq}$ for a reaction presents a problem having the same origin as that concerned with absolute metal-solution potential differences. Experimentally $\Delta H^{\neq}$ can be determined

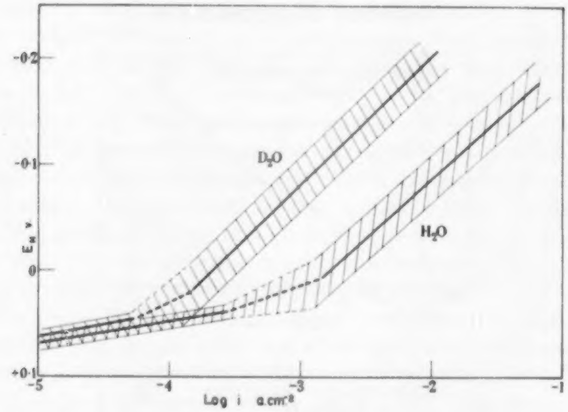

FIGURE 2. Cathodic polarization behaviour of Pd in HCl solution in H_2O and D_2O.

by deriving the exchange currents from polarization measurements by keeping both the working electrode and the reference electrode at the same temperature over a range of temperatures. In this procedure no thermal liquid junction potentials are involved but it is impossible to know how the metal-solution potential difference at the hydrogen reference electrode varies with temperature (the fact that the reversible potential of the hydrogen electrode is arbitrarily considered constant and zero at all temperatures is irrelevant here); thus we can measure $RT^2(\partial \ln i/\partial T)_{\eta=0}$ but not $RT^2(\partial \ln i/\partial T)_{\Delta\phi=0}$. The latter quantity would give the true heat of activation W_0. However, only ΔH_0^*, the apparent heat of activation, is given by the former term. If we attempt to avoid this problem by measuring i_0 as a function of temperature using a reference electrode kept at constant temperature and the working electrode at varying temperatures, a thermal liquid junction potential is included in the measurements again leading to a fundamental uncertainty in W_0. Temkin **(22)** has shown that ΔH^* and W are related as follows

$$\Delta H^* = W - \alpha\, FT\left(\frac{\partial E}{\partial T}\right)_{a_{H^+}} \tag{14}$$

where E is the reversible potential of the hydrogen electrode and α the transfer coefficient determining the value of $d \ln i/d\eta$. The quantity

$$F\left(\frac{\partial E}{\partial T}\right)_{\eta=0}$$

is the entropy change ΔS^0 associated with the "single" electrode reaction

$$H_3O^+ + e_M \rightarrow \tfrac{1}{2}H_2 + H_2O \tag{15}$$

and cannot be thermodynamically evaluated. W_0 hence cannot, in principle, be evaluated from $\Delta H_0^{\ddagger}$ by thermodynamic means. At the reversible potential the equation corresponding to (14) is

$$(16) \qquad \Delta H_0^{\ddagger} = W_0 - \alpha\, T\Delta S^0 + \alpha\, FE = W_0 - \alpha \Delta H^*$$

where ΔH is now the heat content change in reaction (15) and can only be evaluated non-thermodynamically. It is readily seen that ΔH is given by

$$(17) \qquad \Delta \mathrm{H} = \phi_e - \Delta \mathrm{H}_{S,\mathrm{H}^+} - I_{\mathrm{H}} - \tfrac{1}{2}D_{\mathrm{H}_2}$$

when there is zero metal-solution p.d.; in equation (17) ϕ_e is the electronic work function, $\Delta H_{S,\mathrm{H}^+}$ the heat of solvation of H^+, I_{H} the ionization potential of H and D_{H_2} the dissociation energy of H_2. Although the absolute value of ΔH cannot be calculated with any certainty, it is possible to estimate the *change* of ΔH from one metal to another and hence the direction of the *trend* of W_0 values through such a series of metals assuming, with Frumkin **(23)**, that the surface dipole p.d. is similar at related metals in the same solvent, water. An application of this approach will be considered below.

For the same reason that W_0 is inaccessible experimentally, so are the frequency factors A for various mechanisms. In addition, there is the problem of evaluation of θ_{H} which must be known before A can be calculated. Usually **(**cf. **4)** it is reasonable to assume that θ is either near zero (rate-determining I) or near unity (rate-determining II or III). However, in certain cases where I could be rate-determining and the metal is sufficiently catalytic for III to be almost at equilibrium, θ_{H} can be appreciably greater than zero depending on the standard free energy of adsorption of H from gaseous H_2. Limiting calculations for frequency factors may be made for reaction I at Hg assuming **(16)** $\theta_{\mathrm{H}} \rightarrow 0$ and for II, for example, at Ni with $\theta_{\mathrm{H}} \rightarrow 1$. Provided that $\theta_{\mathrm{H}} <$ *ca.* 0.1 in the first case and not very much less than 1 in the second, the uncertainty in the corresponding values of log A will not be very serious. If frequency factors are to have any significance similar to that in the case of non-electrochemical heterogeneous reactions, it appears that they should be calculated at the potential of zero charge ($\Delta\phi_0$) rather than at the reversible potential **(**cf. **24**; **29)** for then at least that part of the metal-solution p.d. arising from excess coulombic charge at the interface is eliminated and frequency factors for the hydrogen evolution reaction at various metals should, in principle, be comparable.

Thus at Hg at $\Delta\phi = \Delta\phi_0$, $\eta = -0.20$ *V.* and $\Delta H^* = 18.8$ kcal mole^{-1} **(25)**. In excess salt with $\zeta \rightarrow 0$ and $C_{\mathrm{H}^+} = 0.1$ *N* the value of the apparent frequency factor

$$\frac{ekT}{h} e^{\Delta S^{\ddagger}/R}$$

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*The sign written here differs from that in Temkin's derivation since we have written reaction (15) with electrons on the L.H.S.

at $\Delta\phi = \Delta\phi_0$ is 3.5×10^9. Correspondingly at Ni, for example, for rate-determining II at $\Delta\phi = \Delta\phi_0$ **(26)**, $\Delta H^{\ddagger} = 6$ kcal mole^{-1}, $C_{\mathrm{H}} \doteqdot 1.7 \times 10^9$ mole cm^{-2} ($\theta \doteqdot 1$) and $C_{\mathrm{H}^+} = 0.1\ N$, the apparent frequency factor is 2×10^{16}. For both these reactions a proton is desolvated with the release of $+31$ e.u. but for reaction I an H atom is also adsorbed with loss of one degree of translational motion while in reaction II an atom is *desorbed* and converted, in combination with the discharged proton, to H_2 mobile in three translational degrees of freedom and having two rotational modes of motion. In the above calculations, apparent heats of activation have been used to calculate A values since the W values are unknown. We can, however, diminish any arbitrariness in this approach by evaluating the *difference* of W values for the reactions I and II considered here and then investigate to what extent this difference can account for the difference of the logarithms of the above A values.

We may write, following Temkin **(22)**,

$$W = W_0 + \beta \Delta V F \tag{18}$$

and split up ΔV into components $\Delta\psi$ and $\Delta\chi$ due to excess charge and surface dipoles, respectively. At the e.c.m. $\Delta\psi = 0$ and

$$W = W_0 + \beta \Delta\chi F. \tag{19}$$

At the e.c.m. potentials of Hg and Ni **(26)**

$$i_{\mathrm{Hg}} = F\left[e\,\frac{kT}{h}\,\mathrm{e}^{\Delta s^{\ddagger}/R}\right](a_{\mathrm{H}^+})_s \mathrm{e}^{-W_0/RT}\,.\,\mathrm{e}^{-\beta\Delta\chi F/RT}(\theta_{\mathrm{H}} \rightarrow 0) \tag{20}$$

and

$$i_{\mathrm{Ni}} = 2F\left[e\,\frac{kT}{h}\;\mathrm{e}^{\Delta s^{\ddagger}/R}\right](a_{\mathrm{H}^+})_s (a_{\mathrm{H}})_s \mathrm{e}^{-W_0/RT}\,.\,\mathrm{e}^{-\beta\Delta\chi F/RT}(\theta_{\mathrm{H}} \rightarrow 1); \tag{21}$$

where the terms $(a_{\mathrm{H}^+})_s$ and $(a_{\mathrm{H}})_s$ are the activities of the indicated species at the surface. Now $W_0 = \Delta H_0^{\neq} + \beta\Delta H$, and indicating reaction I at Hg and II at Ni by the appropriate subscripts we have

$$\ln A_{\mathrm{Hg}} - \ln A_{\mathrm{Ni}} = \ln\left[\frac{2i_{\mathrm{Hg}}}{i_{\mathrm{Ni}}}\right]_{\Delta\psi=0} + \ln(a_{\mathrm{H}})_s + \frac{(\Delta H^{\ddagger}_{0,\mathrm{Hg}} - \Delta H^{\ddagger}_{0,\mathrm{Ni}})}{RT} + \frac{\beta}{RT}(\Delta H_{\mathrm{Hg}} - \Delta H_{\mathrm{Ni}}) \tag{22}$$

where A_{Hg} and A_{Ni} are now the *chemically* significant frequency factors uncomplicated by the voltaic potential difference due to $\Delta\psi$; from equation (17), $\Delta H_{\mathrm{Hg}} - \Delta H_{\mathrm{Ni}} = \phi_{\mathrm{Hg}} - \phi_{\mathrm{Ni}} = -11.5$ kcal mole^{-1} **(27)**. $\Delta\chi$ is assumed (cf. **23**; **29**) to be approximately the same for Hg and Ni but not necessarily zero. This assumption may be more justified for metals having similar lattice structures and electronic properties since the electron asymmetry p.d. at the surface can vary with the metal **(26)**.

Numerical evaluation of the terms in equation (22) gives

$$\log\,(A_{\mathrm{Hg}}/A_{\mathrm{Ni}}) = -\,35. \tag{23}$$

The apparent logarithmic frequency factor ratio calculated above directly from the ΔH^{*} values and the rates at the e.c.m. was

$$\log \frac{3.5 \times 10^{9}}{2 \times 10^{16}} = -6.8.$$

The value given in equation (23) must be regarded as that having the more clearly defined chemical significance in the ordinary kinetic sense; it is apparent that reaction I at Hg has a significantly lower real "probability factor" than that for II at Ni. If the reaction at Ni were assumed to proceed by rate-determining I, the following limiting values of $\log A_{\mathrm{Hg}}/A_{\mathrm{Ni}})$ would be obtained:

$\theta_{\mathrm{H}} \to 0$	$\theta_{\mathrm{H}} = 0.9$	$\theta_{\mathrm{H}} = 0.99$
$+\,5.3$	$+\,4.3$	$+\,3.3$

taking these values of θ_{H} for the nickel electrode and $\theta_{\mathrm{H}} \to 0$ for Hg. Here $\log A_{\mathrm{Hg}}/A_{\mathrm{Ni}}$ has been evaluated for $\theta_{\mathrm{H}} > 0$ at Ni as well as for $\theta_{\mathrm{H}} \to 0$, since at Ni the chemisorption of hydrogen is exothermic (28-32 kcal mole^{-1}) and θ_{H} could be appreciable if III were almost in equilibrium **(33)** with I rate-determining. Thus, the probability factor for reaction I at Hg would be about 10^{4}–10^{5} times that for the *same* reaction at Ni. The difference of the Ni—H and Hg—H bond strengths **(24)** in the final state of I can hardly account for this difference of A for a given mechanism since at room temperature vibrational contributions to the entropy of adsorbed H will be small or negligible. Similarly, at most metals, H is mobile in two dimensions **(28)** so that there should be no important difference in the entropy of adsorbed H on this account. The difference of A values found for Hg and Ni therefore lends some support to the view that there is a difference of mechanism at these metals as indicated by other criteria **(16**; **4**; **30**; **36)**.

6. Other indirect methods for elucidation of reaction mechanism. The most commonly encountered Tafel slopes for the hydrogen evolution reaction have the value $-\,2RT/F$ and for a number of metals where this value is observed, other diagnostic data such as values of the stoichiometric number **(29)** are not always determinable. Thus, it has been of interest to examine possible *indirect* criteria by which, for example, rate-determining I or II can be distinguished under conditions where the Tafel b values are the same.

(i) *Kinetic parameters and metallic properties.* We have shown previously **(30)** that $\log i_{0}$ is dependent upon the electronic work-function ϕ_{e} and the heat of adsorption of H. Two groups of metals exist for which the *sign* of the slopes both of log i_0 *vs.* ϕ_e and log i_0 *vs.* heat of adsorption of H are different. This difference of dependence of rate upon metallic properties between the two groups of metals has been attributed **(30)** to the operation of two different rate-determining mechanisms in hydrogen evolution, viz., I at Hg, Tl, and Pb and II at most of the transition and neighbouring metals which give $d\eta/d \ln i \doteqdot -2RT/F$. The interpretation of this difference of behaviour of these metals has been based in our previous work **(30)** on the principle that H-desorption reactions will tend to be slow at those metals at which H is strongly bound while the H-adsorption reaction I will tend to be fast at such metals (cf. **31**). This assignment of mechanism in the two groups of metals is also consistent, where data are available, with stoichiometric numbers, isotope effects (see below), and surface coverage by H **(16)**. Recently, Parsons **(32)** and Gerischer **(33)** have given theoretical treatments of the dependence of rate upon the free energy of adsorption (ΔG^0) of H and have shown that two directions of dependence of log i_0 upon ΔG^0 for both mechanisms I and II can be obtained. In this work, variations of rate with ΔG^0 are attributed entirely to surface coverage effects, it being assumed that the potential energy profiles at the reversible potential which determine (in part) the free energy of activation are independent of the metal. The validity of this assumption may be tested by plotting (for example for reaction I) the potential energy profiles for various energies of adsorption D_0 of H at the metal as shown in Figure 3

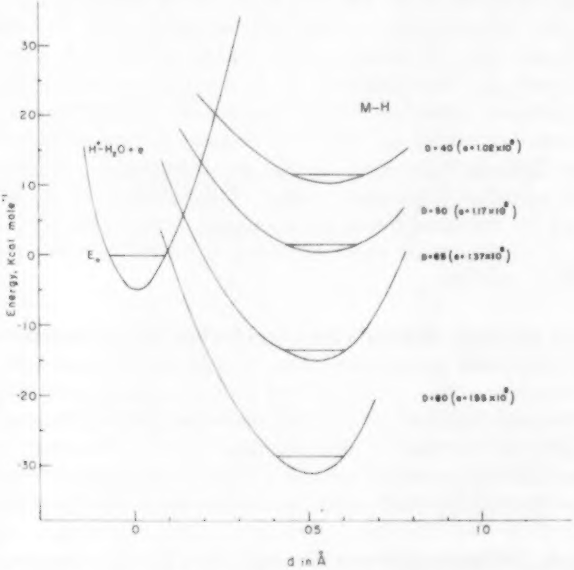

FIGURE 3. Potential energy profiles for reaction I for various MH bond energies (arbitrary).

(the relevant Morse constants *a* are shown in brackets and are based on spectroscopic data for the dependence of bond frequency in diatomic molecules upon dissociation energy (cf. **36**)). Here the levels of the initial and final states are fixed by the method discussed by Temkin (**22**). At the reversible potential, the free energy levels of initial and final states must be identical giving the corresponding profiles shown in Figure 4. In this diagram the *form* of the free energy profile for a given metal is taken as the same as that of the corresponding potential energy profile, as assumed by Parsons (**33**). It is clear that apart from the rounding effect (not shown in Figure 4; cf. the "non-crossing" rule) at the activated state, there are quite important differences of free energy of activation ΔG^{*} depending on the value of the heat of adsorption of H chosen and hence upon the metal. The variation of ΔG^{*} shown in Figure 4 for the various values of D_0 will lead to changes of rate by a factor of about 10^4 a. cm^{-2}. For a considerable number of metals, except Hg, Pb, and Tl which form a separate group, the range of experimental i_0 values is between 10^{-8} and 10^{-4} a. cm^{-2} so that the above effect, arising from differences in free energy of activation at the reversible potential, can account for at least 50 per cent of the range of logarithmic rates. It must therefore be concluded that the effect of variation of M—H bond energy in determining the rates through ΔG^{*} is not negligible. Some experimental evidence in support of this conclusion is discussed below. It may be noted that larger effects than those shown in Figure 4 could arise if the length of the reaction co-ordinate between the minima of the Morse curves had been taken greater than 0.5 Å; the latter figure is the minimum transfer distance consistent with accepted atomic dimensions and probable "thickness" of the double-layer (**8**; **24**).

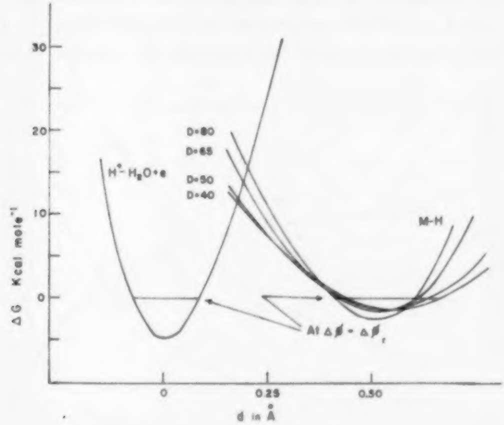

FIGURE 4. Free energy profiles for reaction I at the reversible hydrogen potential based on the potential energy profiles in Figure 3.

(ii) ***Behaviour of alloy electrodes with varying electronic character.*** The kinetics of several heterogeneous reactions have been studied at alloy catalysts and related to the electronic character (*d*-band holes or *d*-character) of the metal. At copper and nickel $d\eta/d \ln i \doteqdot -2RT/F$ and the heat of adsorption of H varies by about 24 kcal mole^{-1} **(34)** from Ni to Cu. Alloys of Cu and Ni are therefore very suitable for examining the dependence of rate and heat of activation for hydrogen evolution upon the changing electronic character of the metal and the associated change of heat of adsorption of H. Thus with Ni there are 0.6 *d*-holes per atom which are filled at the 60 per cent Cu-Ni alloy and the *d*-character of the interatomic bonding varies from 35.7 per cent in Cu to 39.5 per cent in Ni. The unit cells in the two metallic lattices are of the f.c.c. type with a difference of only 0.09 Å between the values of the lattice constants. Any dependence of kinetic parameters upon alloy composition can hence be attributed mainly to electronic effects.

Experimental results to be reported in detail elsewhere **(35)** lead to the values of log i_0 and ΔH_0^* (the apparent heat of activation at $\eta = 0$) shown in Figure 5. The rates are seen to be higher at Ni than at Cu but the heats of activation show an unexpected trend in the reverse direction. In order to interpret these results in terms of *chemically* significant quantities such as metal-hydrogen bond energy it is desirable first to express both the i_0 and ΔH^* data as the corresponding values at the *e.c.m. potential* (cf. **29)** for then primary voltaic effects are diminished to zero and the surface potential effects can be regarded as approximately constant **(23; 29)** in

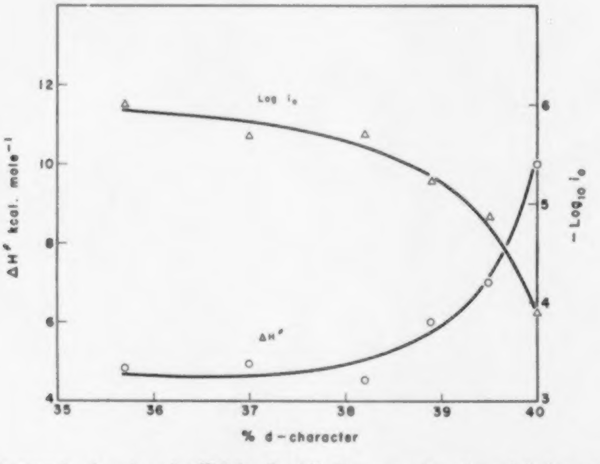

FIGURE 5. Log i_0 and ΔH_0^* for Cu–Ni alloys as a function of *d*-character.

the series of closely related metals. Secondly, it is necessary to examine if the *trend* of the real or true heats of activation from Cu to Ni is similar in direction to that of the apparent heats of activation. This is done by expressing the true value W_0 in terms of the apparent value by means of equation (16) using the ΔH values for reaction (15) as derived from equation (17) in terms of the electronic work functions of the alloys. In this calculation a linear dependence of work function upon composition is assumed and is based on the values of Michaelson **(27)** for Cu ($\phi_e = 4.47$ ev) and Ni ($\phi_e = 4.84$ ev). The trend of the true heats of activation is seen from Figure 6 to be similar to that for the experimental apparent heats. Uncertainty in the absolute position of the upper curve in Figure 6 cannot be avoided for reasons discussed previously but the *relative* positions of the points for each alloy are not, in principle, uncertain so that the *trend* of the true ΔH^* values is known.

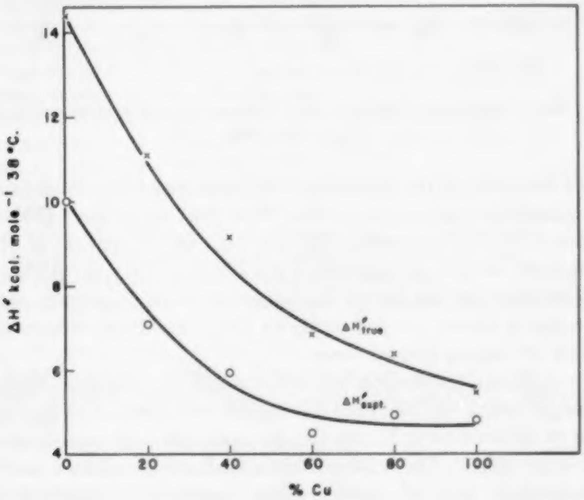

FIGURE 6. Trend of apparent and "true" heats of activation with composition in the series of Cu–Ni alloys.

In correcting the rates and apparent heats of activation to the e.c.m. potential, values of the latter for the various alloys have been deduced from those for Cu and Ni **(26)** assuming the demonstrated linear dependence of the e.c.m. potential upon electronic work function **(26)**. The corrected rates and ΔH^* values are shown in Figure 7 from which it is seen that:

(a) the direction of the trend of both the rates (at the e.c.m. potential) and the heats of activation at the same potential are now kinetically no longer anomalous;

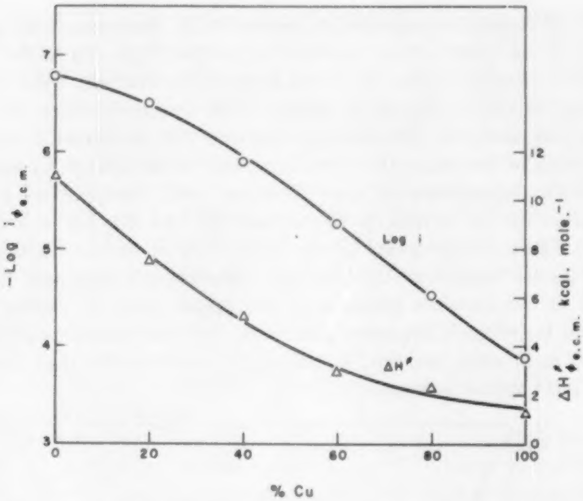

FIGURE 7. Rates and heats of activation for hydrogen evolution corrected to the potential of zero charge.

(b) the direction of the dependence of rates and heats of activation upon heats of adsorption is now consistent with the "atom-ion" **(33)** desorption mechanism II if it is accepted that the heat of adsorption of H at nickel is substantially larger (numerically) than that at copper. Although values in the literature for the heat of adsorption of H at copper show serious discrepancies, a recent careful analysis **(34)** of this problem supports the assignment of values chosen here.

(c) the rates are apparently not determined in a related series of metals by surface coverage effects alone but significant changes of *heat of activation* with heat of adsorption of H can also be demonstrated experimentally.

(iii) *Isotope effects.* The study of isotope effects provides a useful indirect and independent way of investigating reaction mechanisms in electrochemical hydrogen evolution. Full details of experimental and theoretical work have been published elsewhere **(36)** and we shall only mention here, for example, that the observed H/D isotope separation factors S fall into two clearly defined groups having values of S about 3 and 6-7. The soft non-catalytic metals Hg and Pb give the low values while more catalytically active metals give the higher ones. The two groups of values can be predicted theoretically **(36)** in fair agreement with experiment if the rate-determining reaction at Hg and Pb is I and if it is the desorption step II at most of the more noble and catalytic metals. The assignment of mechanism on the basis of isotope effects is hence consistent with that indicated by the other indirect criteria discussed previously.

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